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John H. Margeson, Joseph E. Knoll and M. Rodney Midgett
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Bruce B. Ferguson
Harmon Engineering and Testing Company, Inc.
Auburn, Alabama

Philip J. Schworer
PEI Associates, Inc.
Cincinnati, Ohio

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John H. Margeson, Joseph E. Knoll and M. Rodney Midgett
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Harmon Engineering and Testing Company, Inc.
Auburn, Alabama

Philip J. Schworer
PEI Associates, Inc.
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A manual method for measuring reduced sulfur compounds in kraft pulp mill and sulfur recovery plant emissions was evaluated. The method involves removing SO_2 from the gas stream (if present) with a citric acid-potassium citrate buffer that passes reduced sulfur compounds; thermal oxidation of all reduced sulfur compounds to SO_2; collection of the SO_2 in H_2O_2; and a titrimetric analysis of the H_2O_2 for SO_4^{2-}. A heated filter removes alkaline particulate matter that would produce a negative interference if absorbed by the buffer. When used at kraft pulp mills, the method agrees closely with Reference Method 16, provided that nonregulated reduced sulfur compounds, such as carbonyl sulfide, are not present in the emissions. At sulfur recovery plants, nonregulated reduced sulfur compounds, such as thiophene, are likely to be present in the emissions and will produce a positive bias in the results obtained with this method. The precision of the method ranges from 1 to 7 percent relative standard deviation.

In 1976, the Environmental Protection Agency promulgated reference methods for measurement of total reduced sulfur (TRS) emissions from kraft pulp mills (Method 16) and Claus sulfur recovery plants (Method 15).[1,2] TRS emission standards of 5 and 8 ppm for the recovery furnace and the lime kiln (at kraft pulp mills), respectively, have been promulgated.[3] H_2S is the main TRS compound in the emissions. Emissions from the smelt dissolving tank are also covered by the regulation. All of these sources are part of the chemical recovery process from the pulping operation.[4] TRS was defined as the sum of: H_2S; CH_3SH (methyl mercaptan); $(CH_3)_2S$ (dimethyl sulfide); and $(CH_3)_2S_2$ (dimethyl disulfide) for kraft pulp mills. The emission standard for sulfur recovery plants is 300 ppm TRS and 10 ppm H_2S.[5] To meet the above standard, it was necessary to install a tail gas cleanup unit (based on the Stretford process) before emitting the gas to the atmosphere. These units normally control H_2S, but are not as effective in the control of other compounds. COS (carbonyl sulfide) and CS_2 (carbon disulfide) are the main TRS compounds in the emissions. TRS was defined as the sum of COS, CS_2, and H_2S for Claus sulfur recovery plants.

Since the reference methods had to measure individual sulfur compounds, gas chromatography (GC) separation with FPD detection was chosen as the principle of the methods. In actual field use, it has been found that both methods are difficult to operate successfully, because of the amount of instrumentation and quality control required. Thus, there was a need for a simpler method for measuring TRS compounds. This observation led the National Council of the Paper Industry for Air and Stream Improvement to develop a manual method for measuring TRS compounds.[6] The method involves separation of SO_2 (which is present in the emissions from kraft pulp mills) from TRS compounds by passage of the stack gas through a buffer, thermal oxidation of all four TRS compounds to SO_2, collection of the SO_2 in H_2O_2 solution where it is oxidized to SO_4^{2-}, and analyzing the SO_4^{2-} titrimetrically. The advantage of this method is that it is potentially easier to operate than Methods 16 and 15 and it can be used in place of Method 16. The disadvantage of the method is that individual compound identity is lost and the method does not discrimate against non-TRS compounds that may be present in the emissions and cause a positive interference. For example, under certain conditions, COS has been identified in lime kiln emissions.[4]

This paper presents the results of a laboratory and field evaluation of this method. Most of the work was directed at kraft pulp mill applications.

Mr. Margeson and Dr. Knoll are chemists and Mr. Midgett is chief of the Source Branch, Quality Assurance Division of the Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, NC 27711. Dr. Ferguson is a chemist and was with Harmon Engineering and Testing Company, Inc., Auburn, AL, when this work was carried out. His present address is ATC, Inc., Auburn, AL 36830-4303. Mr. Schworer is a chemist and was with PEI Associates, Inc., Cincinnati, OH, when this work was carried out. His present address is 2100 Fountain Square Plaza, Cincinnati, OH 45202. This paper was submitted for peer review March 7, 1985; the revised manuscript was received September 25, 1985.

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16. ABSTRACT

A manual method for measuring reduced sulfur compounds in Kraft pulp mill and sulfur recovery plant emissions was evaluated. The method involves removing SO_2 from the gas stream (if present) with a citric acid-potassium citrate buffer, that passes reduced sulfur compounds; thermal oxidation of all reduced sulfur compounds to SO_2; collection of the SO_2 in H_2O_2; and a titrimetric analysis of the H_2O_2 for SO_4^{2-}. A heated filter removes a alkaline particulate matter that would produce a negative interference if absorbed by the buffer.

The method is unbiased provided that non-regulated reduced sulfur compounds such as COS (Kraft pulp mills) and thiophene (sulfur recovery plants) are not present in the emissions. If present, these compounds will be oxidized to SO_2 and thereby produce a positive bias. The precision of the method ranges from 1 to 7% relative standard diviation.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Experimental

A schematic diagram of the sampling train is shown in Figure 1. The components of the sampling train up to the oxidation tube are all Teflon. Teflon, rather than glass, was used to avoid losses due to reaction of sulfur compounds with glass. The sample lines and impingers after the oxidation tube are glass. The probe was 0.6-cm O.D. Teflon tubing, and was used in samplings at kraft pulp mills, with the inlet perpendicular to or turned away from the direction of the gas flow. The probe was stabilized by a stainless steel sheath or by taping to a wooden support. The filter for removing particulate matter and the filter holder were Teflon (Savillex Corp., Minnetonka, MN). The body of the Teflon impingers (Savillex) for containing the potassium citrate-citric acid buffer was constructed of threaded segments. This feature allowed the impinger volume to be adjusted depending on the amount of condensate to be collected, thereby preventing the impinger contents from overflowing into the next impinger. Two impingers in series, each containing 100 mL of 1-M potassium citrate-citric acid buffer, followed by an empty impinger, were used unless otherwise noted. The quartz oxidation tube (30 × 2.5 cm) was contained in an electrically heated Lindberg furnace. The remainder of the sampling train was the same as in EPA Method 6.[7] The titrimetric analysis of samples was the same as in Method 6 except that a 10-mL buret with 0.05-mL graduations was used.

The concentration of TRS compounds in N_2, contained in aluminum gas cylinders, was verified by GC/FPD analysis (the GC was calibrated with atmospheres generated from permeation tubes) or by Method 11.[8] The GC/FPD has a lower detectable limit of 0.1 ppm S.

Quality control (QC) was applied to the method by sampling an H_2S atmosphere (generated by flow dilution with air of the contents of an analyzed cylinder) titrating the collected sample, and determining the percent recovery relative to the H_2S concentration sampled. The matrices of the different emissions that were sampled had the compositions shown in Table I.

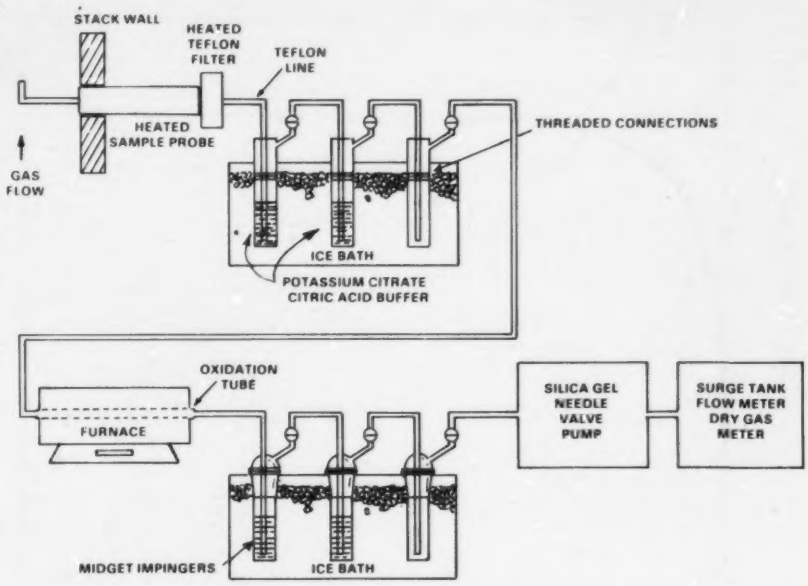

Figure 1. Method 16A sampling system.

Results and Discussion

Previous work at kraft pulp mills[6] showed that all four TRS compounds were rapidly oxidized to SO_2 at 800–1000°C. It has also been shown that the collection efficiency of SO_2 in H_2O_2, contained in a single midgett impinger, was essentailly 100 percent over a wide range of SO_2 concentrations.[9] A number of buffer systems have been examined for their effectiveness to simultaneously absorb SO_2 and pass the four TRS compounds; a potassium citrate-citric acid buffer was the most effective.[10] Based on this background information, a laboratory investigation was initiated to investigate and optimize the sampling variables for sampling emissions at kraft pulp mills.

TRS Oxidation Variables and Buffer Evaluation

The first experiments determined the effect of O_2 concentration, TRS flow rate, and furnace-combustion temperature on TRS oxidation. This was done by generating the appropriate atmosphere by flow dilution of TRS compounds in cylinders with O_2, forcing the diluted gas through the furnace at different flow rates and monitoring the gas stream exiting the furnaces for TRS compounds with a GC/FPD. The results showed that the oxidation was relatively insensitive to flow rate. For example, with flow rates of 1–8 L/min, 7 ppm H_2S was completely oxidized to SO_2 at an O_2 concentration of 1.0 percent v/v and a temperature of 800°C. With all four TRS compounds at 4–7 ppm and the same conditions as above, complete oxidation was obtained at 2.2–5.0 L/min (higher flow rates were not studied). Since the emission sources at kraft pulp mills contain more than 1.0 percent O_2,[4] addition of O_2 to the sample gas stream should not be necessary.

With the effect of oxidation variables established, the next experiments focused on evaluating the potassium citrate-citric acid buffer. To be effective, the buffer must be capable of absorbing SO_2 while passing TRS. If the SO_2 is not absorbed it will, of course, act as a positive interferent.

In aqueous solution, SO_2 dissolves and establishes an equilibrium as follows:

$$SO_2\,(gas) = SO_2\,(aq) \qquad (1)$$

$$SO_2\,(aq) + H_2O \overset{k_1}{=} HSO_3^- + H^+ \qquad (2)$$

$$HSO_3^- \overset{k_2}{=} SO_3^{2-} + H^+ \qquad (3)$$

$$k_1 = 10^{-2};\ k_2 = 10^{-8}$$

The formation of hydrogen ions in reactions (2) and (3) lowers the pH and reduces the solubility of SO_2. Removing the H^+ increases the solubility of SO_2.

H_2S is also soluble in water and es-

Table I. Compositions of the matrices of sampled emissions.[a]

Parameter	Source: Lime kiln	Source: Recovery furnace	Source: Stretford unit
Temperature, °F	130	370	100
Moisture content, % (v/v)		28	7
Oxygen, % (v/v)	8–12	7	<0.5
CO_2, % (v/v)	14	11	

[a] All of the matrices contained particulate matter, the composition of which is discussed in the text.

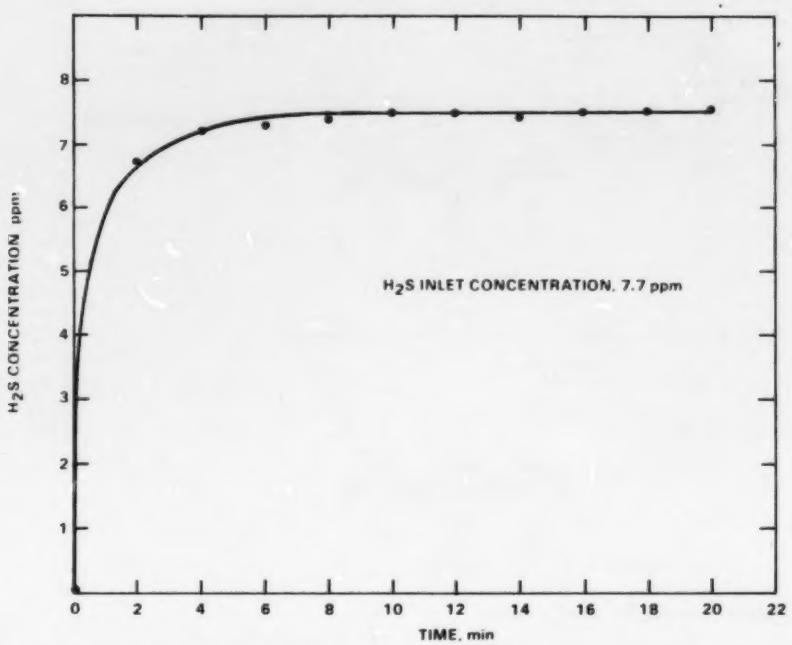

Figure 2. H_2S equilibration rate in potassium citrate-citric acid buffer.

tablishes the following equilibrium:

$$H_2S\ (gas) = H_2S\ (aq) \qquad (4)$$

$$H_2S\ (aq) \overset{k_3}{=} HS^- + H^+ \qquad (5)$$

$$HS^- \overset{k_4}{=} S^{2-} + H^+ \qquad (6)$$

$$k_3 = 10^{-7};\ k_4 = 10^{-13}$$

Removing H^+ in this case produces the undesired result of increasing the solubility of H_2S. For the dissociation of CH_3SH, k_1 is only 10^{-11} and $(CH_3)_2S$ and $(CH_3)_2S_2$ do not dissociate in aqueous solution. Since the solubility of both SO_2 and H_2S is affected by pH, it is necessary to use a solution buffered at a pH where SO_2 is soluble but TRS compounds are not appreciably soluble. Potassium citrate-citric acid at pH 5.5 meets these conditions.

Since TRS losses in the buffer solution are most likely to occur with H_2S, and H_2S is the most prevalent TRS compound in the emissions, H_2S was used in all experimentation with the buffer. The main parameter of interest was the rate at which H_2S reached equilibrium in the buffer solution. This was examined by sampling an atmosphere of 7.7 ppm H_2S in N_2 at 2.0 L/min using the impinger system described in the experimental section and measuring the H_2S concentration at the outlet of the last impinger with a GC/FPD. The results in Figure 2 show that equilibrium was obtained in approximately 10 min. The effect of rapidly changing the H_2S concentration from 5.3 to 20.7 ppm, as might be expected to happen when sampling actual emissions, was also determined. The results in Figure 3 show that the reestablishment of equilibrium was rapid.

The absorptive capacity of the buffer for SO_2 was also determined by sampling an atmosphere of 500 ppm SO_2 in N_2 (which is approximately 10 times the maximum concentration expected in the actual emissions) at 2.0 L/min using only one impinger. The gas stream exiting the impinger was monitored for SO_2 with a GC/FPD. After more than five hours of sampling, no breakthrough of SO_2 occurred.

These results indicate that an equilibrated potassium citrate-citric acid solution is efficient in absorbing SO_2 and passing H_2S and that equilibration time is minimal.

Effect of Particulate Matter on Buffer Performance

Emissions from a lime kiln, in addition to TRS, contain a mixture of $CaCO_3$, $Ca(OH)_2$ and CaO; the particulate matter emissions from a recovery boiler are mainly Na_2SO_4.[4] Both gas streams generally contain 25–35 percent moisture. Thus, the lime kiln, because of the basic particulate matter, represents the greatest challenge in using the method at a kraft pulp mill. Therefore, field testing was initiated at a lime kiln. Sampling times of one and three hours are important with this method, hereafter referred to as Method 16A, because the protocol for determining the relative accuracy, i.e., relative to the reference method, of TRS continuous monitors[11] requires a sampling time of one hour. Demonstration of compliance with new source performance standards requires a sampling time of three hours.

The first field test involved two Method 16A sampling trains operated in parallel at a lime kiln. Each train had a separate probe, the inlet of which was perpendicular to the gas flow in the stack. There were no filters prior to the citrate buffer solutions. Stack gas was pulled through the buffer solution at 2 L/min for 10 min to obtain equilibrium prior to the start of sampling. During sampling, the particulate matter emissions approached those of an uncontrolled source. The results in Table II show that the QC checks before sampling produced an H_2S recovery of approximately 80 percent with both sampling trains. After three contiguous one-hour samples and a subsequent QC sample, there was essentially no change in the QC recovery for train B. However, the QC recovery for train A decreased to 55 percent and the pH of the buffer increased by 0.5 pH unit relative to train B. Also, the three one-hour

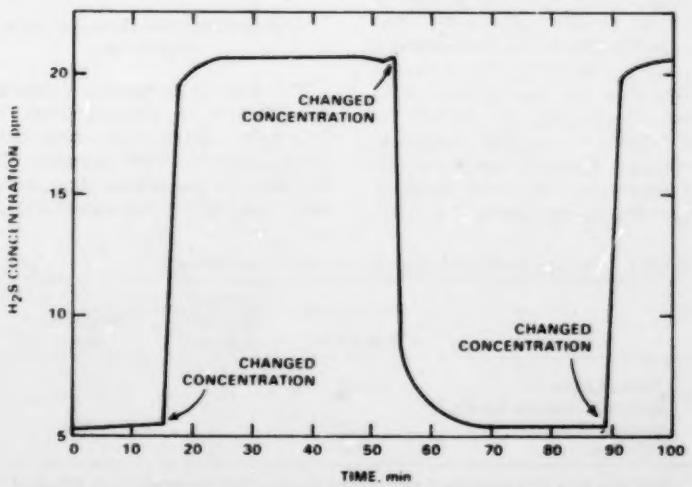

Figure 3. Effect of sudden changes in H_2S concentration on H_2S buffer equilibration.

Table II. Sampling with Method 16A at a lime kiln.

Sample	TRS, ppm		Calculated H_2S conc., ppm
	Train A	Train B	
	Fresh citrate buffer		
QC	6.5 (77%)	7.0 (83%)	8.4 (100%)
Lime kiln, 1h	5.6	5.8	
Lime kiln, 1h	5.5	6.1	
Lime kiln, 1h	4.8	6.2	
QC	5.3 (55%)	7.4 (77%)	9.6 (100%)
pH of citrate buffer	6.6	6.1	

TRS values for train B were similar, but the last one-hour value for train A decreased significantly relative to the first two values.

These results indicate that the buffer in train A absorbed more alkaline particulate matter than in train B (due to an inadvertent difference in probe orientation) and increased the pH such that the TRS-buffer equilibrium shifted, thereby increasing the loss of TRS. In separate samplings, some fine particulate matter that was not wet by the buffer solution was actually collected in the midget impingers. When the samples were titrated, the results were similar to that of the blank, because the SO_4^{2-} was precipitated as $CaSO_4$.

Removal of Particulate Matter from the Gas Stream

The next experiment investigated ways of removing the basic particulate matter from the gas stream. Before actual sampling, both glass and Teflon filter materials were investigated to determine the effect of H_2S sample flow rate on equilibration of the surfaces. This was done by sampling a 4-ppm H_2S in N_2 atmosphere at different flow rates. As expected, equilibration of the glass was much more sensitive to flow rate than Teflon. Therefore, Teflon filters and filter holders were used in all filtration experiments. These experiments involved a field test at another lime kiln in which the effect of probe inlet geometry and Teflon filter porosity on particulate matter removal was evaluated. The first samplings involved determining the ability of an upturned probe, Teflon tubing equipped with a 90° Teflon elbow with the inlet pointed downstream in the stack, to reject particulate matter relative to a straight probe, i.e., no elbow with the inlet perpendicular to the direction of the gas flow. Four Method 16A sampling trains were assembled: two with probes with 90° elbows and two without elbows. Each train contained a heated filter and 0.01 N HCl in place of the buffer. The probes were sheathed in stainless steel to provide in-stack rigidity. Four identical three-hour samples were taken. After sampling was completed, particulate matter in the probes and on the filter was recovered and the dry weight of particulate matter was determined. The results in Table III show that the Teflon elbow-filter combinations collected 30 times less particulate matter than did the probes without elbows. The pH of the HCl solution was essentially unchanged, indicating that no significant amount of particulate matter penetrated the filter. Thus, the upturned probe inlet was efficient in rejecting particulate matter.

The experiments to determine the effect of Teflon filter porosity on the collection of particulate matter involved four Method 16A sampling trains, all with Teflon elbows as the probe inlet. Two trains were equipped with 1–2 μm porosity and two with 20–30 μm porosity Teflon filters. All four trains contained buffer solution and all trains were operated as described above. The results in Table III show that the mass of particulate matter collected was similar in both pairs of trains. The pH of the citrate buffer was essentially unchanged, indicating that no significant amount of particulate matter penetrated either filter. After sampling, the heated filters, containing alkaline particulate matter, were checked for reaction with H_2S by passing a 4-ppm H_2S in N_2 gas over the filters at 2.0 L/min. The H_2S concentration, at the filter outlet, was monitored with a GC/FPD. No loss of H_2S

Table III. Evaluation of particulate matter removal devices at a lime kiln.[a]

Run No.	Probe[b]	Filter[c]	Impinger solution	Particulate matter, mg		
				Probe	Filter	Total
1	90° Teflon elbow, opening turned upward parallel to the direction of gas flow	Glass, 0.3 μm	0.01 N HCl	5	21	26
1	90° Teflon elbow, opening turned upward parallel to the direction of gas flow	Glass, 0.3 μm	0.01 N HCl	6	27	33
1	Teflon tubing, opening perpendicular to direction of gas flow	Glass, 0.3 μm	0.01 N HCl	1025	60	1085
1	Teflon tubing, opening perpendicular to direction of gas flow	Glass, 0.3 μm	0.01 N HCl	884	77	961
2	90° Teflon elbow as in run 1	Teflon, 1–2 μm porosity	Citrate buffer	7	17	24
2	90° Teflon elbow as in run 1	Teflon, 1–2 μm porosity	Citrate buffer	6	17	23
2	90° Teflon elbow as in run 1	Teflon, 20–30 μm porosity	Citrate buffer	9	11	20
2	90° Teflon elbow as in run 1	Teflon, 20–30 μm	Citrate buffer	7	17	24

[a] Sampling trains operated at a flow rate of 2.0 L/min for 3 h.
[b] Average probe temperature, 220°F.
[c] Average filter temperature, 250°F. The filter holder was of the same material as the filter.

Table IV. Comparison of Methods 16A and 16 at a lime kiln.

Run	TRS concentration, ppm Method 16A	Method 16	Difference, %
3[a]	10.5 ± 0.4[c] (3.6%)	11.2 ± 7.1 (63%)	−6.3
4[b]	15.0 ± 0.3 (2.1%)	14.0 ± 3.4 (24%)	+7.1

[a] Values corrected for H_2S QC recovery of 83.4% (Method 16A) and 58.7% (Method 16). This correction is justified, because H_2S was the only TRS compound in the stack.
[b] Values corrected for H_2S QC recovery of 92.5% (Method 16A) and 83.4% (Method 16).
[c] One standard deviation.

was observed. If the filters had not been heated during sampling, moisture condensation would have occurred on the filter and the resulting alkaline conditions would have resulted in a loss of H_2S, as discussed earlier.

Comparison of Method 16A with Method 16 at a Kraft Pulp Mill

The next field testing involved comparing Method 16A with Method 16 at a lime kiln and a recovery furnace to determine if Method 16A was biased relative to Method 16. Since Method 16 samples intermittently, the TRS emission level must be reasonably stable, i.e., no large change in concentration, to permit a meaningful comparison with a completely integrated method, like Method 16A. In the comparison at the lime kiln, three Method 16A sampling trains and one Method 16 sampling train were operated simultaneously such that all trains sampled the same atmosphere. The optimum version of Method 16A, as shown in Figure 1, was used; the Teflon-particulate filter had a porosity of 1–2 μm. Two comparisons were made, one for 60 min (run 3) and one for 30 min (run 4). The results in Table IV show that the average concentrations obtained with the two methods agreed within 6–7 percent. A statistically valid t-test to test the significance of this difference could not be carried out because of two factors: the instability of the emissions during sampling and the lack of a representative value for the precision of Method 16. The instability of the source is evidenced by the Method 16 standard deviations of 63 and 24 percent for the two sampling periods. Considering the large variation in the emissions, the observed difference of 6–7 percent between the two methods is probably not significant.

The comparison at a recovery furnace was carried out with two Method 16A sampling trains and one Method 16 sampling train. Since particulate matter (mainly Na_2SO_4) collected in the buffer would not affect the pH, no filters were used in the sampling trains. The comparison consisted of four contiguous one-hour samplings. The results in Table V show excellent agreement between the two Method 16A sampling trains at low TRS levels, 2 ppm; the QC recovery after completion of sampling was near 100 percent. The Method 16 values (<1 ppm) were significantly lower than the Method 16A data, however. The reason for this difference could not be determined, and there were no QC recovery data available for Method 16. However, a recent comparison of Methods 16A and 16 at a recovery furnace showed that there was no significant difference between the two methods.[12]

Table V. Comparison of Methods 16A and 16 at a recovery furnace.[a]

Sample	TRS ppm, Method 16A Train A	Train B	Method 16, TRS ppm	Calculated H_2S conc., ppm
Recovery furnace, 1 h	2.4	2.6	0.85	
Recovery furnace, 1 h	1.6	2.2	0.93	
Recovery furnace, 1 h	2.2	2.2	0.78	
Recovery furnace, 1 h	2.5	2.5	0.71	
Mean	2.2	2.4	0.82	
QC	3.7 (102%)	3.9 (106%)		3.65 (100%)

[a] Probe inlet was perpendicular to the direction of the gas flow. The sampling train did not contain a filter.

Method 16A Precision

As a result of sampling at lime kilns and recovery furnaces, five separate estimates of the precision of Method 16A were obtained. These data are summarized in Table VI. The results show that the relative standard deviation ranged from 1 to 4 percent at TRS concentrations of 3–15 ppm. Thus, the precision of Method 16A is excellent.

Field Testing at a Claus Sulfur Recovery Plant

COS is the main TRS compound in the emissions from this source. Method 15, the reference method for measurement of these emissions, is based on the same principle as Method 16. Therefore, it was decided to investigate application of the principle of Method 16A to measurement of these emissions. Reduced sulfur compounds are emitted from a Stretford sulfur recovery unit under reducing conditions[13] and there is no SO_2 present (<0.1 ppm as measured by Method 6). Therefore, the buffer is not needed, but O_2 must be added to the gas stream to allow oxidation of TRS to SO_2. If the moisture content of the stack gas is low enough (~7%), as was the case at this particular source, the H_2O_2 containing midget impingers will have sufficient volume to collect the condensate. At sources with higher moisture contents, the potassium citrate-citric acid buffer that is used with Method 16A can be used to collect the condensate. Concerning oxidation of TRS, it was found that a temperature of 1100–1200°C was necessary to ensure 100 percent oxidation of COS to SO_2. The fact that a higher temperature is required to oxi-

Table VI. Precision of Methods 16A and 15A.

Source sampled	Sampling time[a], h	Mean TRS conc.[b], ppm	Relative standard deviation, %
Recovery furnace	3	7.2	2.6
Recovery furnace	3	3.4	0.8
Lime kiln	1	11.7	3.6
Lime kiln	1	15.4	3.6
Lime kiln	0.5	8.0	2.8
Stretford sulfur recovery unit	3	40.6	2.8
Stretford sulfur recovery unit	1	41.0	6.9

[a] At 2.0 L/min.
[b] Average of triplicate sampling trains.

dize COS (when compared to the oxidation of H_2S) is to be expected, because the activation energy for the oxidation of COS is higher than that for H_2S. A Teflon filter is necessary to remove particulate matter, because the particulate matter contains metals that could interfere in the titrimetric analysis. The angled-upturned probe is not necessary, because the mass of particulate matter collected is small.

The modified version of Method 16A described above, hereafter referred to as Method 15A, and Method 15 were compared by simultaneous measurement of emissions from a Stretford sulfur recovery unit. The experimental design was the same as that used in the comparison of Methods 16A and 16. The GC results showed that the TRS emissions were stable. However, a compound not covered by the TRS regulation, later identified as thiophene (C_4H_4S), appeared in all of the Method 15 chromatograms, and the Method 15A results were approximately 30 percent higher than Method 15. Thus, thiophene was oxidized to SO_2 by Method 15A and was therefore a positive interferent relative to Method 15 when the latter results are based solely on the regulated TRS compounds. Since thiophene and other nonregulated sulfur compounds are present in petroleum,[14] interference from nonregulated sulfur compounds can be expected in this application of Method 15A.

Most TRS emissions from Stretford-recovery units are low relative to the standard. In the above samplings, for example, the average of three separate Method 15A samplings gave a TRS value of 38 ppm. Since the actual emissions are considerably lower than the standard, Method 15A may have some utility in measuring TRS emissions from sulfur recovery units, despite the interference from nonregulated TRS compounds.

Conclusions

Method 16A agrees closely with Method 16, provided that nonregulated reduced sulfur compounds, such as COS, are not present in the emissions. The precision of Method 16A, 1–4 percent relative standard deviation, is more than adequate for its use in relative accuracy determinations. Method 15A can be used to measure reduced sulfur compound emissions at sulfur recovery plants, but nonregulated sulfur compounds, such as thiophene, produce a positive interference.

Acknowledgment

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